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SYNTHESIS AND STRUCTURE OF SOME TRIPHENYLTIN(IV) DITHIOCARBAMATE COMPOUNDS

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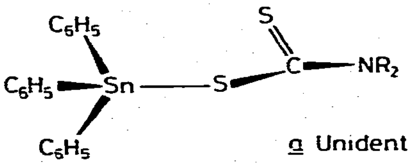
Summary

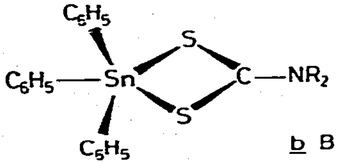
A low temperature synthesis is described for the preparation of organotin dithiocarbamate compounds (including *N*-cyclic and *N*-monosubstituted derivatives) in which the products have low levels of the usual sulfide impurities. IR spectra cannot differentiate unambiguously the bidentate and anisobidentate modes of bonding of the dithiocarbamate ligands with the metal, but ^{1}H NMR spectra of the $(C_6H_5)_3Sn$ moiety exhibit (*o-mp*) shift differences which can, in part, be attributed to anisobidentate bonding. The effect of solvents on shift values is also indicative of this unsymmetric chelation.

Introduction

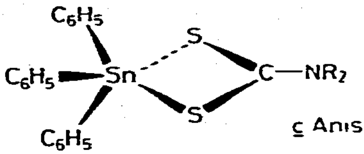
The first report of clearly defined phenyltin dithiocarbamate compounds came from Kupchik and Calabretta [1] in 1965. An extension of this work was reported by Bonati and Ugo [2a] in 1967, who, besides identifying reliable syntheses, attempted to determine which physical methods could distinguish between the two possible covalent bonding models for the dithiocarbamate ligand in these complexes: the unidentate (ester-type structure, Fig. 1a) and the bidentate (chelating dithiocarbamate; Fig. 1b). Since that time, a good deal of interest has centered around this structural aspect of organotin dithiocarbamate chemistry. Honda et al. [3] used infrared spectroscopy to conclude (as did Bonati and Ugo [2]) that the dithiocarbamate ligand was chelating in a series of methyltin compounds. However, when the molecular structure of $(CH_3)_2Sn(Cl)S_2CN(CH_3)_2$ was determined [4], the chelation of the dithiocarbamate ligand was found to be unsymmetrical, with Sn—S bond lengths of 2.48 and 2.79 Å. Similar results were also found [5—7] for $(CH_3)_3SnS_2CN(CH_3)_2$, $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$ and $(C_6H_5)_3SnS_2CN(C_2H_5)_2$, while $Sn[S_2CN(CH_3)_2]_4$ and $Sn[S_2CN(C_2H_5)_2]_4$ were shown to contain both bidentate and unidentate ligands [8]. This situation of one "normal" and one "weak" Sn—S bond is con-



a Unidentate.



b Bidentate.



c Anisobidentate.

Fig. 1.

sistent with data found in Mössbauer spectroscopy and has led to the coining of the term "anisobidentate ligand" to describe the function of the dithiocarbamate [9] (Fig. 1c).

This paper reports investigations on the synthesis and structure of a number of triphenyltin(IV) dithiocarbamate compounds. A low temperature method for preparing all the reported complexes in good yield and high purity has been devised. Evidence is presented to indicate that the dithiocarbamate ligand also displays anisobidentate character in these complexes.

Abbrevations employed in the text are as follows: dithiocarbamate, DTC; methyl, Me; ethyl, Et; propyl, Pr; butyl, Bu; cyclohexyl, c-Hex; benzyl, Ben; pyrrolidyl, Pyr; piperidyl, Pip; morpholyl, Morph; phenyl, Ph.

Experimental

Synthesis

(i) Sodium salts of dithiocarbamate derivatives were prepared by mixing acetone solutions of carbon disulfide, the appropriate amine and concentrated aqueous sodium hydroxide [10] at 0—10°C. These were crystallized from acetone/petroleum ether (except $NaDTC(n\text{-}Bu)_2$ and $NaDTC(c\text{-}Hex)_2$).

(ii) Triphenyltin chloride was prepared from tetraphenyltin and tin tetrachloride [11].

(iii) Chlorodiphenyltin(IV) *N,N*-diethyldithiocarbamate was obtained by the method of Kupchik and Calabretta [1] and recrystallized from diethyl ether (m.p. 144.0—144.5°C, Lit. [1] 143—145°C).

(iv) Triphenyltin(IV) acetate was prepared from triphenyltin chloride and lead acetate [12] (m.p. 118°C, lit. [12] 119—120°C).

(v) Tetrakis (*N,N*-dimethyldithiocarbamato)tin(IV) and dichlorobis(*N,N*-dimethyldithiocarbamato)tin(IV) were obtained from the reaction of $SnCl_4$ with four and two mole equivalents, respectively, of NaDTC(Me)$_2$ in acetone, analogous to the procedures reported by Bonati et al. [2]. The precipitated NaCl was filtered off, the solvent evaporated and the products recrystallized from acetone or diethyl ether. The compound $Cl_2Sn[DTC(Pyr)]_2$ was obtained using a similar procedure.

(vi) Chlorotris(*N,N*-dimethyldithiocarbamato)tin(IV) was prepared by warming a mixture of $SnCl_4$ and NaDTC(Me)$_2$ in acetone in 1/3 mole ratio. The mixture was filtered and a dilute solution of NaDTC(Me$_2$) was added dropwise to the warm filtrate until the solution became slightly turbid. The solution was filtered once more and the acetone evaporated to yield orange crystals (m.p. 248–248.5°C. Found: C, 20.6; H, 3.4; Cl, 6.8; Sn, 23.4. $C_9H_{18}N_3S_6ClSn$ calcd.: C, 20.9; H, 3.5; Cl, 6.9; Sn, 23.3%).

(vii) Cresolthiolatotriphenyltin(IV), $(C_6H_5)_3SnSC_6H_4$-*p*-CH_3 was prepared by mixing equimolar solutions of triphenyltin chloride and *p*-toluenethiol in CCl_4 at room temperature then adding the same molar concentration of aqueous NaOH with vigorous stirring [13a]. Stirring was continued for 3 h and the CCl_4 solution separated. Evaporation of the solvent yielded the compound (m.p. 102–104°C, lit. [13b] 103–105°C).

The compound $(C_6H_5)_3$SnS-n-Pr was prepared by a similar method.

(viii) Triphenyltin dithiocarbamate compounds were all prepared by the same method: the procedure outlined for the $(C_6H_5)_3$SnDTC(Pyr) derivative is typical.

Approximately 100 cm^3 A.R. grade acetone were placed in a reaction flask, fitted with two dropping funnels and an efficient stirrer, and the temperature lowered to −30°C. One dropping funnel contained 5 mmol of triphenyltin chloride dissolved in acetone and the other 5 mmol of sodium DTC(Pyr) in acetone. These solutions were added simultaneously and dropwise to the reaction flask, with stirring, over a period of 2 h. The mixture was filtered rapidly and the acetone vacuum distilled off at about 10°C. The solid thus obtained was dissolved in sodium-dried diethyl ether and the solution filtered, if cloudy. Partial evaporation of the ether using a stream of air produced crystals which were again recrystallized from diethyl ether. Yields were of the order of 70%, and the microanalytical data of some of the compounds are given in Table 1.

TABLE 1

MICROANALYTICAL DATA [a] FOR SOME OF THE COMPOUNDS PREPARED BY THE LOW TEMPERATURE METHOD

Compound	Analysis (Found (calcd.) (%))				
	C	H	S	N	Sn
$Ph_3SnDTC(n\text{-}Bu_2)$	58.52 (58.38)	5.96 (5.95)	11.7 (11.5)	2.19 (2.52)	21.5 (21.6)
$Ph_3SnDTC(Pyr)$	55.52 (55.53)	4.76 (4.63)	13.6 (12.9)	2.76 (2.82)	24.7 (24.2)
$Ph_3SnDTC(i\text{-}Pr_2)$	56.92 (56.93)	5.52 (5.50)	12.6 (12.1)		

[a] Microanalysis by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

TABLE 2

MASS SPECTRA

Compound	Probe temper-ature (°C)	Parent peak	*m/e* ^{120}Sn values			Sulfide peak
			R_2SnL^{+} [a]	Ph_3Sn^+	SnL^+	
$Ph_3SnDTC(Et_2)$	170	499	422 [c]	351	—	655 $(Ph_2Sn)S(Ph_3Sn)^+$
$Ph_3SnDTC(i\text{-}Pr_2)$	170	527	450	351	—	655 $(Ph_2Sn)S(Ph_3Sn)^+$
$Ph_3SnDTC(n\text{-}Bu_2)$	110	—	478	351	323	306 (Ph_2SnS^+)
$Ph_3SnDTC(Pyr)$	150	—	420 [c]	351	266	—
$Ph_3SnDTC(Pyr)$	170	497	420 [c]	351	266	655 $(Ph_2Sn)S(Ph_3Sn)^+$
$Ph_3SnDTC(Pip)$	200	511	534	351	279	732 $(Ph_3Sn)_2S^+$
$Ph_3SnDTC(Me)(Benz)$	200	547	470	351	316	—
$Ph_2Sn(Cl)DTC(Et_2)$	200	457	422 [d]	—	—	409 $(Ph_2Sn)S(PhSn)^+$
$Ph_3SnDTC(H)(n\text{-}Pr)$	80	—	331 [b, e]	351	254	306 (Ph_2SnS^+)
$n\text{-}Bu_3SnDTC(H)(n\text{-}Pr)$	70	—	368 [e]	—	254	500 $(Bu_2Sn)_2S^+$

[a] R = Ph, or n-Bu. [b] This peak corresponds to $PhSnL^+$ in this case. [c] Mass spectrum also contains *m/e* 309, corresponding to Ph_2SnCl^+. [d] Mass spectrum also contains *m/e* 380, corresponding to $PhSn(Cl)L^+$. [e] Mass spectrum also contains *m/e* 234, corresponding to Bu_2Sn^+.

^{1}H NMR spectra

All spectra were recorded using a Varian T-60NMR spectrometer operating at 60 MHz, and at ambient temperature. Solvents used were A.R. grade CCl_4, CS_2, Benzene, and $CDCl_3$. Spectra were also recorded at 5, 10, 15, 20 and 25% w/v concentrations, but no noticeable difference could be observed for a given solvent.

Mass spectra

These were obtained using a Jeol-D100 Mass Spectrometer over the probe temperature range 100—200°C. A parent peak was detected for all compounds which were heated above 150°C. Table 2 lists the *m/e* values for the ^{120}Sn isotope.

IR spectra

These were recorded with a Perkin—Elmer 457 Grating Spectrometer, using KBr pressed disks, and calibrated with polystyrene film.

Results and discussion

(i) Syntheses

In preparations of the type reported in this work, the sulfide, $[(C_6H_5)_3Sn]_2S$, often occurs as an impurity. For the *N*-monoalkyl dithiocarbamate compounds, this occurs through the reactions [1,2a]:

$$2\ Ph_3SnCl + 2\ NaS_2CN(H)R \rightarrow (Ph_3Sn)_2S + CS_2 + (RNH)_2CS + 2NaCl$$

$$2\ Ph_3SnDTC(H)R \xrightarrow{\Delta} (Ph_3Sn)_2S + CS_2 + (RNH)_2CS$$

However, the mass spectra of both the *N,N*-dialkyl and *N*-monoalkyl dithiocarbamate compounds, give evidence of sulfide impurity. The *N*-cyclic dithiocarbamate compounds, which might be considered as similar to the dialkyl derivatives, contain more sulfide than the latter. Thus, two possibilities arise: either both the *N*-monoalkyl and the *N,N*-dialkyl compounds are unstable at the probe temperature (120—200°C), or the sulfide is formed by a process different from the thermal decomposition postulated.

Two other preparative methods were tried, involving widely differing temperatures. The compound $Ph_3SnDTC(Et_2)$ was prepared by the addition of a solution of $NaDTC(Et_2)$ to a solution of Ph_3SnCl which was kept at —30°C. After 3 h, the solution was filtered and the solvent (acetone) air-evaporated. Mass spectra of the solid product from this process indicated over 5% $(Ph_3Sn)_2S$ present. Recrystallization from diethyl ether reduced the sulfide level to 2—3%. This indicates that the sulfide may be formed during preparation.

The second method consisted in refluxing acetone solutions of Ph_3SnCl and NaDTC(Pyr), for 3—4 hours. The product melted at 142—146°C (cf. 172°C for $Ph_3SnDTC(Pyr)$) and exhibited a ^{1}H NMR spectrum containing poorly-resolved peaks, these peaks being coincident with those of a pure sample of Ph_3SnDTC-(Pyr). Thus, a product containing a considerable amount of impurity was obtained by this method. Obviously, the synthesis of these complexes is complicated by side reactions which appear to be influenced by both temperature and relative concentrations of starting materials.

The low temperature modification outlined herein yields products with relatively low sulfide impurity levels, sharp melting points and well-resolved ^{1}H NMR spectra. In addition, the procedure is satisfactory for *N*-cyclic derivatives and for *N*-monosubstituted derivatibes. Bonati and Ugo reported that these latter compounds were unable to be prepared by the conventional syntheses [2a].

The mass spectra obtained contain the peaks expected for these complexes. The spectra show the peak pattern due to the polyisotopic nature of tin *, and the *m/e* values reported correspond to the ^{120}Sn isotope. The parent peak is easily detected and the largest peak is always that due to the fragment produced by the loss of one phenyl group. The values shown in Table 2 do not represent all the peaks in the spectra, but only those that confirm the presence of both compound and impurities. The temperatures shown were selected to ascertain if the relative abundance of the sulfide is much greater at elevated temperatures. This could not be established, but it was noticed that, whenever more unreacted triphenyltin chloride was present, a greater amount of the sulfide was detected.

(ii) Infrared spectra

Relevant IR frequencies are listed in Table 3. The spectra of these compounds are complicated by peaks due to the aromatic rings and assignments are difficult as in the case of $Ph_3SnDTC(c\text{-}Hex_2)$. The values shown are very similar to those found for other dithiocarbamate complexes [1b].

Since the work of Bonati and Ugo [2a], attempts have been made to deduce the "denticity" of the ligand by using the $\nu(C{\cdots}N)$ and $\nu(C{\cdots}S)$ regions in the IR spectra. For example the compounds $Se[DTC(Et_2)]_2$ and $Ti[DTC(Et_2)]_4$ show a splitting in the $\nu(C{\cdots}N)$ region [17]. Also, $Sn[DTC(Et_2)]_4$ and $Sn[DTC(Me_2)]_4$ show a splitting in this region, and both compounds contain both unidentate and bidentate ligands. The complex $ClSn[DTC(Me_2)]_3$, in which both unidentate and bidentate ligands might also be expected, displays a very strong, broad band at 1542 cm^{-1}. Spectra of all the compounds in this work contain one strong band in this region, and the values do not follow the trend of decreasing frequency with increasing chain length of the *N*-alkyl substituent which has been reported for some complexes [16,18].

Generally, an increase in $\nu(C{\cdots}N)$ is accompanied by a decrease in $\nu(C{\cdots}S)$, and is similar to the trend observed [3] for the series of complexes $Me_2Sn(X)$-$DTC(Me_2)$ (X = Cl, Br, I). This trend may be linked with variations in the relative electron density between tin and the dithiocarbamate ligand. The region around 1000 cm^{-1} contains two bands from the phenyl rings, and no other peak except the $\nu(C{\cdots}S)$ reported could be detected. The 1000 cm^{-1} region has been shown to be reliable for determining whether the ligand is bidentate or unidentate only if a splitting of the peaks of >20 cm^{-1} is obtained [19]. Since some $\nu(C{\cdots}S)$ values are around 980 cm^{-1}, another peak at or near 1000 cm^{-1} would certainly have been detected if it was present. It may then be safely concluded that no splitting of the required magnitude exists in this region. It is remarkable that $ClSn[DTC(Me_2)]_3$ contains a singlet $\nu(C{\cdots}N)$ but a doublet

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* The naturally occurring tin isotopes are: ^{112}Sn, 0.96; ^{114}Sn, 0.66; ^{115}Sn, 0.35; ^{116}Sn, 14.30; ^{117}Sn, 7.61; ^{118}Sn, 24.03; ^{119}Sn, 8.58; ^{120}Sn, 32.85; ^{122}Sn, 4.72; ^{124}Sn, 5.94%. Source: ref. 15.

TABLE 3

RELEVANT IR FREQUENCIES (ν, cm^{-1}) OF PHENYLTIN DITHIOCARBAMATE COMPOUNDS

s, strong; m, medium; w, weak; (sh), shoulder; (br), broad.

Compound	M.p. (°C)	ν(C=N)	ν(C=S)	ν(Sn–S)[a]	ν(Sn–C)[b]
$Ph_3SnDTC(Me_2)$	131–132[c]	1515s	975s	390w	270m 325w
$Ph_3SnDTC(Et_2)$	135[d]	1487s	980s	390m	279m
$Ph_2Sn(Cl)DTC(Et_2)$	144[e]	1517s	985s	390s	270w
$Ph_3SnDTC(i\text{-}Pr_2)$	166–168	1471s	990m	390w	270w
$Ph_3SnDTC(n\text{-}Bu_2)$	112–114	1497s	985m	390w	270w
$Ph_3SnDTC(c\text{-}Hex_2)$	179	—	950m	410w	270w
$Ph_3SnDTC(Morph)$	176	1469s	1000s	360w	270w
$Ph_3SnDTC(Pyr)$	170–172	1473s	1000s	355m	255vw
$Ph_3SnDTC(Pip)$	135–136	1493s	980m	368w	270vw
$Ph_3SnDTC(Me, Ben)$	102–104	1500s	—	390w	275w
$Ph_3SnDTC(H, Ben)$	126[f]	1500s	975s	340w	310w
$Ph_3SnDTC(H, n\text{-}Pr)$	85–86[g]	1520s(br)	965(sh) 980(sh)	378m	295w
$ClSn[DTC(Me_2)]_3$	248	1542s(br)	964s 970s(sh)	385s 375s	315w (Sn–Cl[b])
$Sn[DTC(Me_2)]_4$	300(dec.)	1522s 1492s	978s	390m	
$Cl_2Sn[DTC(Me_2)]_2$	266	1538s	964s	380m	280w (Sn–Cl[b])
$Cl_2Sn[DTC(Pyr)]_2$	298(dec.)	1513s	990m	348m	310m (Sn–Cl[b])

[a] Ref. 3. [b] Ref. 20. [c] Lit. m.p. 136–137°C, ref. 2a. [d] Lit. m.p. 132–133°C, ref. 2a. [e] Lit. m.p. 143–145°C, ref. 1. [f] Lit. m.p. 124–126°C, ref. 1. [g] Lit. m.p. 86°C, ref. 14a.

(separation 14 cm^{-1}) $\nu(C{=}S)$, whereas $Sn[DTC(Me_2)]_4$ shows splitting of $\nu(C{=}N)$ but not of $\nu(C{=}S)$. The compounds $Cl_2Sn[DTC(Me_2)]_2$ and $Cl_2Sn[DTC(Pyr)]_2$, which are expected to contain bidentate ligands, do not show splitting in either $\nu(C{=}N)$ or $\nu(C{=}S)$.

(iii) ^{1}*H NMR spectra*

Results of the ^{1}H NMR studies are summarized in Table 4.

(a) Phenyl proton resonances. The phenyl group of peaks are similar to those exhibited by some monosubstitued benzenes [21] and also to $PhSnCl_3$ and $PhSiCl_3$ [22]. The difference in chemical shift between the *ortho*-proton resonance and that for the *meta*- and *para*-protons is affected by the ligand bonded to the Ph_3Sn entity. Examples of monosubstituted benzenes and phenyltin complexes with similar (*o-mp*) shift values are shown in Table 5.

The dithiocarbamate ligand exerts a greater effect on the Ph_3Sn portion of

TABLE 4

^{1}H NMR SPECTRA (CHEMICAL SHIFTS (δ, PPM) RELATIVE TO TMS INTERNAL STANDARD)

Compound	Solvent	δ(N—CH)	δ(N—C—R)	δ_o	$\delta_{m,p}$	$\delta_{o\text{-}mp}$
Ph_3SnCl	$CDCl_3$	—	—	7.65	7.45	0.20 [a]
$Ph_3SnS(n\text{-}Pr)$	CCl_4	—	—	7.58	7.40	0.18
$Ph_3SnSC_6H_4\text{-}p\text{-}CH_3$	CCl_4	—	—	7.40	7.40	0.00
$Ph_3SnDTC(Me_2)$	CCl_4	3.57	—	7.80	7.45	0.35
$Ph_3SnDTC(Et_2)$	CCl_4	3.92	1.30	7.75	7.40	0.35
	CS_2	3.67	1.20	7.60	7.30	0.30
	Benzene	3.33	0.86	7.9	—	—
	$CHCl_3$/Benzene	3.52	0.96	7.80	—	—
$Ph_3SnDTC(i\text{-}Pr_2)$	CCl_4	—	1.46	7.73	7.40	0.33
	$CS_2/CDCl_2$	4.65	1.40	7.60	7.25	0.35
	$CDCl_3$(20% w/v)	4.80	1.50	7.80	7.40	0.40
$Ph_3SnDTC(n\text{-}Bu_2)$	CCl_4	3.80	0.91—1.8	7.60	7.26	0.34
	CS_2	3.70	1.0—1.8	7.53	7.26	0.27
	Benzene	3.55	0.85—1.6	7.8	—	—
$Ph_3SnDTC(c\text{-}Hex_2)$	CCl_4	—	1.0—2.0	7.75	7.42	0.33
$Ph_3SnDTC(Ben_2)$	CCl_4	5.16	7.46	7.83	7.50	0.33
$Ph_3SnDTC(H, Ben)$	CCl_4	4.70	7.30	7.75	7.36	0.39
	$CDCl_3$	4.70	7.30	7.80	7.40	0.40
$Ph_3SnDTC(H, n\text{-}Bu)$	CCl_4	3.50	0.9—1.5	7.81	7.43	0.38
$Ph_3SnDTC(Me, Ben)$	CCl_4	3.45	5.20, 7.36	7.70	7.30	0.40
	CS_2	3.20	5.00	7.53	7.22	0.31
	Benzene	2.90	4.70	7.8	—	—
$Ph_3SnDTC(Pyr)$	CCl_4	3.80	2.10	7.70	7.40	0.30
	CS_2	3.60	1.85	7.53	7.25	0.28
	Benzene	3.26	1.13	8.0	—	—
$Ph_3SnDTC(Pip)$	CCl_4	3.95	1.63	7.64	7.30	0.34
	Benzene	3.60	1.0	8.0	—	—
$Ph_3SnDTC(Morph)$	CCl_4	4.20	3.80	7.75	7.40	0.35
$Ph_2Sn[DTC(Et_2)]_2$	CCl_4	3.78	1.50	7.75	7.25	0.50
$Ph_2Sn(Cl)DTC(Et_2)$	CCl_4	3.75	1.34	7.91	7.31	0.60
	$CHCl_3$/Benzene (1/1, 10% conc.)	3.47	1.00	—	—	—
	CS_2	3.76	1.30	7.85	7.33	0.52
$Ph_3SnOOCCH_3$	$CDCl_3$	δ(C—CH_3)	2.12	7.73	7.45	0.28

[a] Ref. 22, value given as 0.22 ppm.

TABLE 5

EXAMPLES OF MONOSUBSTITUTED BENZENES AND PHENYLTIN COMPLEXES WITH SIMILAR (*o*-*mp*) SHIFT VALUES

Compound	(*mp*) shift (ppm)	(*o*) shift (ppm)	(*o*-*mp*) shift (ppm)
$Ph_3SnSC_6H_4CH_3$	7.40	7.40	0.0
Ph_3SnS-n-Pr	7.40	7.58	0.18
Ph_3SnCl	7.45	7.65	0.20
$Ph_3SnOOCCH_3$	7.45	7.73	0.28
$Ph_3SnDTC(Et_2)$	7.40	7.75	0.35
$Ph_2Sn[DTC(Et_2)]_2$	7.25	7.75	0.50
$Ph_2Sn(Cl)DTC(Et_2)$	7.31	7.91	0.60
PhCH=NPh	7.34	7.87	0.53
PhBr	7.13	7.41	0.28
$PhSSCH_2CH_3$	7.10	7.50	0.40
$PhCCl_3$	7.34	7.83	0.49

the molecule than other sulfur ligands, chloride or acetate (see Fig. 2). Signals in the phenyl proton region (shown in Fig. 3) consist of an A_2B_2C pattern from each phenyl ring. Results of decoupling of each grouping within the phenyl protons for the compounds $Ph_2Sn(Cl)DTC(Et_2)$, $Ph_3SnDT(n\text{-}Bu_2)$, and $Ph_3SnDTC(Me_2)$ also are shown in Fig. 3.

In the monosubstituted benzenes, the (*o*-*mp*) shift difference is attributed to inductive and anisotropic effects of the substituents. Benzaldehyde is an example of a shift difference due mainly to anisotropic deshielding, whereas

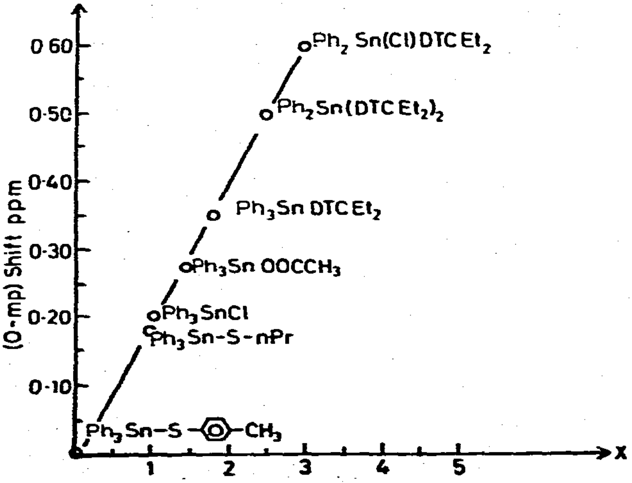


Fig. 2. The effect of different ligands on the (*o*-*mp*) shift value for phenyl tin complexes.

$$X = \frac{(o\text{-}mp)\ \text{shift for the complex}}{(o\text{-}mp)\ \text{shift for } Ph_3SnCl}$$

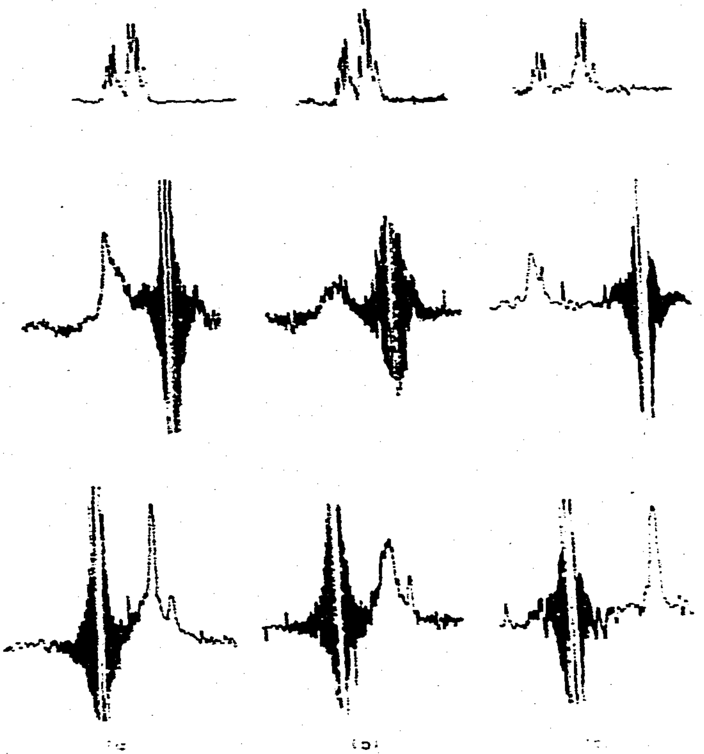


Fig. 3. The phenyl region of the ^{1}H NMR spectra of (a) $Ph_3SnDTC(Me_2)$, (b) $Ph_3SnDTC(n\text{-}Bu_2)$, and (c) $Ph_2Sn(Cl)DTC(Et_2)$. Decoupling of each set of resonances is illustrated below the original spectrum.

nitrobenzene is an example in which inductive deshielding is operative. The spectra in Fig. 3 show the *ortho* peaks at lower field. Integration of each group of peaks does not give the expected 2/3 ratio but a series of values over the range 1/2 to 2/3. The reason for this is not known. Perhaps the effects of the ligand are not the same within each of the phenyl groups.

The ^{1}H NMR spectra of this series of complexes is consistent with the ligand having anisobidentate chelation. With this arrangement, the molecular structure should be distorted tetrahedral, the ligand occupying one apex of the tetrahedron, but the closer approach of the second sulfur atom distorting the arrangement of phenyl groups. The weakly bonded sulfur might be expected to exert a field effect [23], somewhat analogous to a tightly held solvent molecule. The effect would be most pronounced at the *ortho* position, causing these protons to resonate at lower field. In addition, the weakly bound sulfur atom may interact with the tin, possibly via some type of p_π—d_π overlap. Any increase in the electron density of the outer orbitals of tin arising from such an interaction would influence the π-electrons of the phenyl ring. It is relevant in this context that the spectrum of $Ph_3SnSC_6H_4\text{-}p\text{-}CH_3$ shows no (*o-mp*) shift difference for the Ph_3Sn entity, yet produces increased J_{AB} and $J_{A'}$ values for the $SC_6H_4CH_3$ moiety (compared to $HSC_6H_4CH_3$). This suggests that the Sn—S bond contains

TABLE 6

RESONANCES OF SUBSTITUENTS (X) ON NITROGEN

Group (X)	δ(—X—CH$_2$—R) (ppm) [a]
C(O)OR	2.10
C(O)NR$_2$	2.05
C(O)R	2.40
NR$_2$	2.50
I	3.15
N$^+$R$_3$	3.40
NCS$_2$—Metal	3.5—3.9 in CCl$_4$
OH	3.54
OPh	3.90

[a] Values obtained from ref. 24.

sufficient π-character to influence all four aromatic groups in the complex, thus facilitating the distribution of electron density within these rings to bring about the observed spectrum.

The spectrum of Ph$_2$Sn(Cl)DTC(Et)$_2$ contains a very large (*o-mp*) shift difference. This may be attributed to two related causes: (1) the interaction between the Ph$_2$Sn and the CS$_2$ portions of the molecule, and (2) the withdrawal of electron density by the chlorine, strengthening (1) and thus causing the *ortho* position to be further deshielded. The (*o-mp*) shift difference for this complex is much larger than that for PhSnCl$_3$, thus negating a simple electron withdrawal mechanism, such as that postulated [22] for PhSnCl$_3$.

(b) The substituents bonded to nitrogen. The methylene proton resonances of the substituents on nitrogen occur in the range 3.5—3.9 ppm in CCl$_4$ solvent. These values are high in comparison with the values for other groups (see Table 6) and are higher than that for N$^+$R$_3$ in which the nitrogen carries a full positive charge.

The calculated group electronegativity [25] for the DTC(Et$_2$) ligand is 2.6 (Pauling scale) and the C$\cdots$N bond possesses 15% ionic character [26]. (A value of 13—15% ionic character for C$\cdots$N was obtained from ^{1}H NMR spectra in CCl$_4$). These values indicate that simple electronegativity considerations and the partial positive charge on nitrogen should produce a chemical shift for the methylene protons of around 3 ppm. Obviously, the larger values obtained can be attributed to diamagnetic anisotropic deshielding brought about by the delocalized π-electrons of the dithiocarbamate ligand.

Pronounced high field shifts in CS$_2$ and benzene solvents are obtained (Table 4). The theory of solvent effects [27] predicts that rod-shaped solvent molecules such as CS$_2$, whose largest diamagnetic susceptibility is along the rod axis, would assume a configuration parallel to the DTC ligand and thus cause a low field shift. Likewise, flat disk-shaped solvents such as benzene would lie parallel to the ligand and exert a high field shift. However, both CS$_2$ and benzene cause high field shifts relative to CCl$_4$ (Table 4). This would be consistent when considering the S-atoms of the CS$_2$ molecule being attracted to a relatively positive nitrogen atom and repelled by the slightly negative sulfur atoms of the DTC ligand, resulting in the CS$_2$ molecule assuming a configuration almost perpendicular to

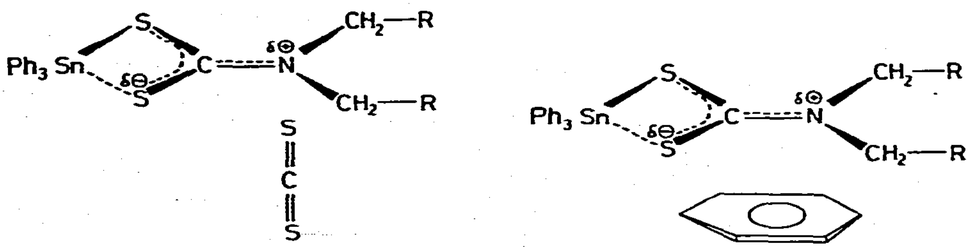
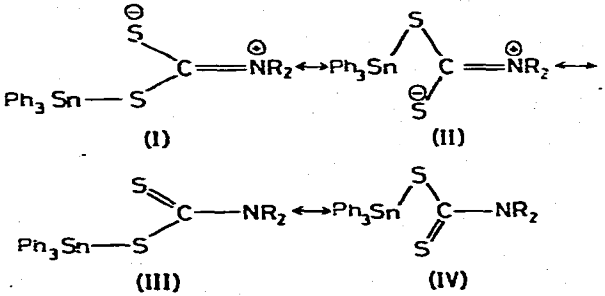


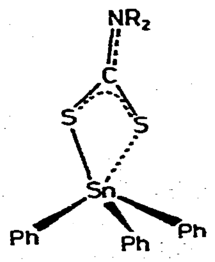
Fig. 4. Postulated interactions of solvent molecules with the dithiocarbamate ligand in the complex $Ph_3SnDTC(R_2)$. (a) CS_2, (b) C_6H_6.

the flat DTC ligand (Fig. 4). Carbon disulfide has a higher dielectric constant than either CCl_4 or benzene and again, the electric field effect [27,28] should cause the protons to absorb at a lower field than either CCl_4 or benzene. The fact that it does not, also suggests that the bonding between tin and the DTC ligand is unsymmetrical.

Conclusion

The results indicate that the complexes studied do not possess a bidentate or unidentate dithiocarbamate ligand. The ^{1}H NMR data especially suggests an unusual interaction between the tin atom and the ligand. This interaction may be viewed as one sulfur atom weakly coordinated to the tin, possibly through π-overlap of the empty d orbitals of tin and the p orbitals of sulfur. The one weakly coordinating sulfur together with one normal tin—sulfur bond results in the so-called anisobidentate behaviour of the ligand. The structure is represented by the canonical forms I—IV, and the overall structure by V.





(V)

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